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REMINERALIZING ADHESIVE DENTAL FILM  
[Remineralisierende Dental-Klebefolie]

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[0001] The invention relates to an adhesive film which has a certain adhesion to the surface of a tooth or to the gum and is soluble and can swell in water, and into which a fine-particulate calcium salt which is poorly soluble in water is intercalated as the remineralizing ingredient.

[0002] Not only cleaning agents, for example toothpastes or mouthwashes, are used to care for the teeth and keep them healthy. Lozenges or chewing gum preparations which have a longer residence time in the mouth are also suited to delivering certain agents to the gum or surface of the tooth. Finally, it has already been suggested that adhesive films which adhere to the gum or surface of the tooth be provided with agents against caries or parodontitis.

[0003] One of the first stages of dental caries is lesions in the tooth enamel and open dentin channels (so-called Tomes pits) which are caused by processes of dissolution under the influence of acid-forming bacteria. The opening of the dentin channel becomes noticeable for example due to the sensitivity of the neck of the tooth to temperature fluctuations. While only pain symptoms are controlled by additives of desensitizing agents, attempts have already been made to prevent formation of these lesions on the tooth surface using additives which reduce apatite solubility. Recently, suggestions have also been made to reduce existing damage by remineralizing oral hygiene agents. Thus, it has been proposed by Chow and Brown (in J. Dent. Res., 54 (1975) 65-70) that dicalcium phosphate-dihydrate be used to remineralize the dentin. US 4,097,558 discloses a mouthwash with a remineralizing action which

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\* Claim and paragraph numbers correspond to those in the foreign text.

was saturated with  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ .

[0004] EP 0 165 454 B1 proposes hydroxyl apatite or fluorapatite in fine particulate form (less than 4 micron particle diameter) as a component of oral hygiene agents.

[0005] EP 0 381 193 A2 discloses films for application to the oral mucosa which can contain a topical agent, for example also sodium fluoride or potassium nitrate.

[0006] WO 95/33441 A1 describes phosphate-free compositions which contain fine-particulate (colloidal) metal compounds, for example of yttrium, cerium, aluminum or zirconium for treatment of hypersensitive teeth and which are also to be applied in the form of oral adhesive plasters.

[0007] Therefore the object was to find an effective application form for calcium salts with a remineralizing action, especially phosphates, fluorides, fluorophosphates and hydroxyl and fluorapatite which causes local remineralization of the damaged tooth enamel.

[0008] This object was achieved as claimed in the invention by an adhesive dental film for local, remineralizing tooth treatment, consisting of a carrier material which adheres to the tooth and which is soluble or swellable in water, and active ingredients intercalated in it, the active ingredients being contained as a fine-particulate calcium salt which is poorly soluble in water, selected from phosphates, fluorides, fluorophosphates and mixtures thereof which can optionally also comprise hydroxyl ions, carbonate ions or chloride ions.

[0009] The carrier film can consist of any solid, flexible material which can dissolve or swell in water. Suitable materials are

preferably natural or synthetic polymers which are softened with water and/or water-miscible solvents. One example of this material is a gelatin which is softened by water and glycerin, for example according to US 3,444,858. Other examples of suitable carrier materials according to WO 00/18365 A1 are for example pullulan, hydroxypropyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, carboxymethyl cellulose, sodium alginate, xanthene gum, tragacanth gum, guar, acacia gum, gum arabica, amylose, hydroxypropyl starch, dextrin, pectin, chitin, chitosan, levan, collagen, zein, gluten, soy protein, casein, polyvinyl pyrrolidone, polyvinyl alcohol, polyethylene glycol, polyacrylic acid, methylmethacrylate/acrylic acid copolymer and mixtures thereof. In one preferred version of the invention the carrier component is a water-soluble or water-swellaable natural or synthetic polymer material, selected from plant and microbial gums, gelatin, cellulose ethers, copolymers of acrylic or methacrylic acid and esters of acrylic or methacrylic acid, polyvinyl alcohol, partially saponified polyvinyl acetate, polyvinyl pyrrolidone and mixtures thereof.

[0010] In the composition of the carrier material, what is important is mainly that the active ingredients are released from the carrier in a controlled manner over a longer time interval, that therefore the carrier material does not break down or dissolve too rapidly in the mouth under the action of saliva and the active ingredient is swallowed before it can act on the tooth or gum.

[0011] The disintegration or dissolution of the carrier material can be delayed by various methods and the release of the active ingredients can thus be controlled in a specific manner. These measures are for example crosslinking of water-soluble polymers, the addition of

less water-soluble polymerizates, the addition of water-repellant components, for example magnesium stearate, or, as is suggested in WO 99/04764 A1, the use of proteins or cellulose ethers which have been crosslinked with tannic acids or tannin.

[0012] Carrier films are produced from a suitable carrier material using known processes, by producing a solution of the polymer or polymer mixture, dissolving or dispersing the active ingredients in it and drying this solution or dispersion in a thin layer on a nonadherent, for example a silicone-coated, substrate. After the solvent is evaporated the finished film can be detached from the substrate and optionally cut to a size which is suitable for application to the teeth.

[0013] Calcium salts which are poorly soluble in water are defined as those salts which are soluble in water at 20°C to less than 0.1% by weight (1 g/l). These suitable salts are for example calcium hydroxyphosphate ( $\text{Ca}_5[\text{OH}(\text{PO}_4)_3]$ ) and hydroxyl apatite, calcium fluorophosphate ( $\text{Ca}_5[\text{F}(\text{PO}_4)_3]$ ) and fluorapatite, fluorine-doped hydroxyl apatite of composition  $\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F})$  and calcium fluoride ( $\text{CaF}_2$ ) or fluorite or fluorspar and other calcium phosphates such dicalcium, tricalcium or tetracalcium phosphate ( $\text{Ca}_2(\text{P}_2\text{O}_7)$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Ca}_4\text{P}_2\text{O}_9$ , oxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$ ) or nonstoichiometric hydroxyl apatite ( $\text{Ca}_{5-1/2(x+y)}(\text{PO}_4)_{3-x}(\text{HPO}_4)_x(\text{OH})_{1-y}$ ).

[0014] The remineralizing ingredient is preferably a fine-particulate calcium salt which is poorly soluble in water and which is selected from hydroxyl apatite, fluorapatite, and mixtures thereof, since the tooth material whose restoration is the objective of remineralization consists roughly 95% of hydroxyl apatite.

[0015] Those poorly water-soluble calcium salts have proven especially advantageous which have a particle fineness of 10-300 nm (nanometers). Here particle fineness is defined as the diameter of the particles in the direction of their greatest extension. The average particle fineness relates to a value which has been averaged over the volume. These calcium salts can be produced for example according to the process known from DE 198 58 662 A1 in the form of rod-shaped primary particles with thicknesses of 5-50 nm and lengths of 10-150 nm.

[0016] In the biological process of formation of the tooth enamel and of the support tissue of the bone, hydroxyl apatite is deposited in an orderly manner on the protein matrix in the tooth or bone which consists primarily of collagen. The formation of the hard and loadable mineral structure is controlled by so-called matrix proteins which are formed from collagen and other proteins which are attached to the collagen and thus cause a controlled mineralization process, so-called biomineralization.

[0017] Proteins are also used as protection colloids which are adsorbed on the surface of the nanoparticles and hinder them in coagulation and agglomeration and slow down crystal growth. Even in remineralization of damaged tartar what is important is that no uncontrolled crystal growth take place which could form only a looser crystal structure. Rather the crystal growth should be slowed down and should proceed in a controlled manner by proteins as the protective colloid so that a dense and relatively strong crystal structure can be formed.

[0018] In one preferred version the adhesive dental film as claimed in the invention furthermore contains a protein component

selected from proteins, protein decomposition products and derivatives of proteins or protein decomposition products.

[0019] Proteins can be any proteins regardless of their origin, therefore both animal and plant proteins. Suitable animal proteins are for example collagen, fibroin, elastin, keratin, albumin and casein. Suitable plant proteins are for example wheat and wheat germ proteins (gluten), rice protein, soy protein, oat protein, pea protein, almond protein and potato protein. Individual proteins such as for example yeast protein or bacteria proteins are also suitable.

[0020] Proteins which are preferred as claimed in the invention are animal products such as collagen, keratin and casein.

[0021] According to another preferred embodiment the protein can originate from a plant or marine source.

[0022] Protein decomposition products are those products which can be obtained by hydrolytic, oxidative or reductive decomposition of water-insoluble proteins into oligostructures and polypeptide structures with lower molecular weight and with improved water solubility.

[0023] Hydrolytic decomposition of water-insoluble proteins is the most important decomposition method; it can take place under the catalytic influence of acids, alkalis, or enzymes. Mainly those protein decomposition products are preferably suited which are not further decomposed than necessary to achieve solubility in water.

[0024] Among the less decomposed protein hydrolysates is for example gelatin which is preferred within the framework of this invention and which can have molar masses in the range from 15000 to 25000 D. Gelatin is a polypeptide which is obtained preferably by



hydrolysis of collagen under acid (type A gelatin) or alkali (type B gelatin) conditions. The gel strength of gelatin is proportional to its molecular weight, i.e. a more strongly hydrolyzed gelatin yields a solution of lower viscosity. The gel strength of gelatin is given in Bloom numbers. In enzymatic splitting of the gelatin the polymer size is greatly reduced; this leads to very low Bloom numbers.

[0025] Derivatives of proteins and protein decomposition products are defined as chemically modified proteins or protein hydrolysates which can be obtained for example by acylation of free amino groups, by attachment of ethylene oxide or propylene oxide and hydroxyl groups, amino groups or carboxyl groups or by alkylation of hydroxyl groups of the protein or protein decomposition product or a hydroxyalkyl derivative thereof, for example with epoxypropyl trimethylammonium chloride or 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride.

[0026] In one especially preferred version the protein component is selected from among gelatin, casein, their hydrolysates and mixtures thereof. The adhesive dental film as claimed in the invention can consist for example mainly of a protein component, for example, of gelatin or collagen, as a carrier material. But if the carrier material is another material, for example a vegetable gum, a single cell biopolymer (xanthene gum, pullulan), a cellulose ether or starch ether, a polyvinyl pyrrolidone or a mixture of cellulose ether, polyvinyl acetate and polyacrylic acid, preferably one protein component should be contained in it in an amount of at least 1 % by weight, preferably 1 - 20% by weight.

[0027] Another especially preferred embodiment consists in that the active ingredient is a composite material of calcium salt which is

poorly soluble in water and a protein component, selected from protein, protein decomposition products, and derivatives of proteins or protein decomposition products. Composites are compound materials which comprise poorly soluble calcium salts and protein components and constitute microscopically heterogeneous, macroscopically but homogeneously appearing aggregates in which the primary particles of the calcium salts are present associated with the skeleton of the protein component. The proportion of protein components in these composite materials is between 0.1 and 60% by weight, but preferably between 1.0 and 20% by weight relative to the weight of the composite material.

[0028] The production of composite materials from hydroxyl apatite and collagen is described for example by R.Z. Wang et al., J. Mater. Sci. Lett. 14 (1995), 490. The hydroxyl apatite particles which are present there have a particle fineness of 2 - 10 nm and therefore belong to the region of amorphous or partially x-ray amorphous substances. Hydroxyl apatite nanoparticles are better suited which have a clearly detectable crystalline morphology with particle fineness which is therefore in the range of 10 - 300 nm. Likewise, composites are better suited in which fine-particulate, poorly soluble calcium salts with particle finenesses of 10 - 300 nm together with fine-particulate proteins, protein hydrolysate or derivatives thereof form a three-dimensional structure such that the fine-particulate calcium salts are deposited on the protein structure, more or less three-dimensionally mirror it. Composite materials consisting of these preferably suitable nanoparticulate calcium salts and protein components lead to especially effective biomineralization.

[0029] Composite materials which are suitable as claimed in the invention can be produced by precipitation from aqueous solutions of water-soluble calcium salts with aqueous solutions of water-soluble phosphate and/or fluoride salts in the presence of protein components.

[0030] This takes place preferably such that the protein components in pure, dissolved or colloidal form are added to the alkali aqueous phosphate salt solution and/or fluoride salt solution or the alkali solution of the calcium salt prior to the precipitation reaction. Alternatively, the protein components are present in pure, dissolved or colloidal form and then are mixed in succession in any sequence or at the same time with the alkali calcium salt solution and the alkali phosphate salt solution and/or fluoride salt solution.

[0031] In the production process the individual components can fundamentally be combined in any possible sequence. The alkalizing agent is preferably ammonia. In all precipitation reactions of this type the pH value for the precipitated system should be above  $\text{pH} = 5$ .

[0032] Another version of the production process consists in that precipitation is done from an acid solution of a water-soluble calcium salt together with a stoichiometric amount of a water-soluble phosphate salt and/or fluoride salt or from an acid solution of hydroxyl apatite with a pH below 5, preferably at a pH below 3, by raising the pH with an aqueous alkali or ammonia to a value above 5 in the presence of protein components.

[0033] Another process version consists in that nanoparticulate calcium salts in pure or dispersed form or dispersions of nanoparticulate calcium salts which have been produced by precipitation reactions from aqueous solutions of water-soluble calcium salts and

aqueous solutions of water-soluble phosphate salts and/or fluoride salts are mixed with protein components, the latter preferably in dissolved or dispersed form, and any sequence can be chosen for the addition.

[0034] Preferably a solution or dispersion of the protein component is present and a dispersion of the nanoparticulate calcium salt is added.

[0035] In all processes during which precipitation of apatite takes place, it is recommended that the pH be kept above 5.

[0036] In all the indicated production processes, the resulting dispersion of the composite material as required can be separated by processes known to one skilled in the art, such as for example filtration or centrifugation, from the solvent and the other components of the reaction mixture, and can be isolated by subsequent drying, for example by freeze drying, in a solvent-free form.

[0037] In all production processes the solvent is preferably water, but in individual steps of production it can also be organic solvents such as for example alcohols with 1 to 4 C atoms or glycerin.

[0038] In one special embodiment of the invention the fine-particulate, calcium salt primary particles or the fine-particulate calcium salt primary particles which are present in the composite materials can be jacketed by one or more surface modification means.

[0039] In this way for example the production of composite materials can be facilitated in those cases in which the nanoparticulate calcium salts can be poorly dispersed. The surface modification agent is adsorbed onto the surface of the nanoparticles and changes them such that the dispersability of the calcium salt

increases and agglomeration of the nanoparticles is prevented.

[0040] Moreover, surface modification can influence the structure of the composite materials and the loading of the protein components with the nanoparticulate calcium salt. In this way, when using composite materials it is possible in the remineralization process to influence the progression and speed of the remineralization process.

[0041] Surface modification agents are substances which physically adhere to the surface of the fine particles, but do not chemically react with them. The individual molecules of the surface modification agents which are absorbed on the surface are essentially free of intermolecular bonds among one another. Surface modification agents are especially dispersants. Dispersants are also known to one skilled in the art under the terms tensides and protective colloids. Suitable tensides or polymer protective colloids can be taken from German patent application DE 198 58 662 A1.

[0042] Production of the composite materials as claimed in the invention, in which the primary particles of the calcium salts are surface-modified, can take place as described above using analogous precipitation methods, but precipitation of the nanoparticulate calcium salts or composite materials taking place in the presence of one or more surface modification agents.

[0043] Preferably first the surface modified nanoparticulate calcium salts are produced by a precipitation reaction between the aqueous solutions of phosphate salts and/or fluoride salts in the presence of surface modification agents. These salts can then be purified of accompanying products of the reaction mixture, for example by concentration under reduced pressure and subsequent dialysis. By

removing the solvent, a dispersion of the surface modified calcium salt with a solid portion can also be produced at will. Then, by adding the protein components in pure, dissolved or colloidal form, in turn the sequence of addition not being critical, and if necessary an afterreaction at elevated temperature, preferably in the range between 50 and 100°C and for an interval from 1 to 100 minutes, the composite material is formed from the surface-coated calcium salt and protein components.

[0044] For production of the adhesive dental film as claimed in the invention, the active ingredient, therefore the fine-particulate calcium salt which is poorly soluble in water, or preferably the composite material of the poorly soluble calcium salt and a protein component, is added to the still liquid solution of the carrier material in water or aqueous alcohol. For this reason the active agent can be used as a nonaqueous and solvent-free powder or also as an aqueous or aqueous-alcohol dispersion. Finally, the dispersion obtained here is dried in a thin layer on a nonadhesive substrate. The amount added depends on how much of the active ingredient is to be contained in the finished adhesive dental film. In one preferred version of the invention the active ingredient is contained in an amount of 0.1 - 10% by weight in the adhesive dental film which is ready to use.

[0045] In addition to the remineralizing, fine-particulate calcium salt which is poorly soluble in water and which is contained as claimed in the invention, other active ingredients which are necessary for healthy teeth or gums and are compatible with the carrier material can be contained. These other active ingredients are for example;

- caries-inhibiting fluorine compounds, for example sodium fluoride,

- tin fluoride, or sodium monofluorophosphate,
- antitartar agents, for example organophosphonates, such as 1-hydroxyethane-1,1-diphosphonic acid, phosphonopropane-1,2,3-tricarboxylic acid (Na salts), 1-azacycloheptane-2,2-diphosphonic acid (Na salt),
  - desensitizing ingredients such as potassium nitrate or oil of cloves (eugenol),
  - vulnerary agents and anti-inflammatories such as for example allantoin, urea, azulene, chamomile ingredients, rhodanide,
  - deodorants and antimicrobials such as for example chlorohexidine, hexetidine, and bromochlorophene.

[0046] Other adjuvants to improve organoleptic properties can also be contained, for example;

- aromatic oils such as for example peppermint oils, oil of curled mint, eucalyptus oil, anise oil, fennel oil, caraway oil, fruit aroma and synthetic aromatic oils,
- sweeteners such as for example saccharin-sodium, acesulfam-K, Aspartame<sup>R</sup>, sodium cyclamate, stevioside, thaumatin, sucrose, lactose, maltose, fructose or glycyrrhizin,
- dyes and pigments.

[0047] The following examples will explain the subject matter of the invention in detail:

#### Examples

##### 1. Production of protein solutions and dispersions

###### 1.1 Type A gelatin

[0048] 10 g of type A gelatin (gelatin obtained by acid hydrolysis of pigskin) were mixed with 100 ml water and boiled once using

microwaves.

### 1.2 Type A gelatin and casein

[0049] 10 g of type A gelatin were mixed with 100 ml water and 10 ml of the supernatant of a casein solution which was saturated at 20°C and then centrifuged at 5000 rpm and subsequently boiled once using microwaves.

### 1.3 Hydrolysate of type A gelatin

[0050] 10 g of type A gelatin were mixed with 100 ml water and the alkali protease Savinase (manufacturer: Novo Nordisk) in a feed concentration of 0.005% enzyme dry substance relative to the dry substance of the gelatin. After 20 hours stirring at 20°C boiling was done once using microwaves.

### 1.4 Hydrolysate of type A gelatin and casein

[0051] 10 g of type A gelatin and 1 g of casein were mixed with 100 ml H<sub>2</sub>O, hydrolyzed overnight at room temperature with the alkali protease Savinase (manufacturer: Novo Nordisk) in a feed concentration of 0.005% enzyme dry substance relative to the dry substance of the protein components, then boiled once using microwaves and subsequently filtered.

### 1.5 Type B gelatin

[0052] 10 g of type B gelatin (gelatin obtained by acid hydrolysis of cowhide) were mixed with 100 ml water and boiled once using microwaves.

### 1.6 Type B gelatin and casein

[0053] 10 g of type B gelatin were mixed with 100 ml water and 10 ml of the supernatant of a casein solution which was saturated at 20°C and then centrifuged at 5000 rpm and subsequently boiled once using



microwaves.

#### 1.7 Hydrolysate of type B gelatin

[0054] 10 g of type B gelatin were mixed with 100 ml water and the alkali protease Savinase (manufacturer: Novo Nordisk) in a feed concentration of 0.005% enzyme dry substance relative to the dry substance of gelatin. After 20 hours stirring at 20°C boiling was done once using microwaves.

#### 1.8 Hydrolysate of type B gelatin and casein

[0055] 10 g of type B gelatin and 1 g of casein were mixed with 100 ml H<sub>2</sub>O, hydrolyzed overnight at room temperature with the alkali protease Savinase (manufacturer: Novo Nordisk) in a feed concentration of 0.005% enzyme dry substance relative to the dry substance of the protein components, then boiled once using microwaves and then filtered.

### 2. Production of composite materials by precipitation reactions in the presence of protein components

#### 2.1 Composite material of hydroxyl apatite and type A gelatin

[0056] 2.21 g of calcium chloride were dissolved in 137 ml completely softened water, the temperature was raised to 25°C, and the solution was set to pH = 11 with a 25% by weight aqueous ammonia solution. With vigorous stirring then 20 ml of the protein solution which was produced according to Example 1.1 and which was heated in a water bath to 30-40°C were added. Subsequently an aqueous solution of 1.58 g diammonium hydrogen phosphate in 26 ml completely softened water which had been raised to a temperature of 25° C and set to pH = 11 with a 25% by weight ammonia solution was slowly added dropwise within 1 hour. In doing so precipitation of the composite material took place.

The pH at the start of the drip interval was 10.4 and was held at a value of roughly 10 by re-dosing the ammonia solution. After 20 h reaction time (25°C, with stirring) the pH value of the aqueous suspension dropped to 9.5. The precipitated composite material, centrifuged off at 5000 rpm, was washed with completely softened water with a temperature of roughly 30-40°C and freeze-dried. The yield was 2.2 g of composite material whose elementary analysis yielded a carbon content of 2.3%; this corresponds to a content of protein material of 5.6% by weight relative to the total amount of composite material.

#### 2.2-2.8 Composite materials of hydroxyl apatite and other protein components

[0057] Composite materials of hydroxyl apatite and the protein components described under 1.2 to 1.8 are obtained analogously to as described in Example 2.1.

### 3. Production of composite materials by intermingling dispersions of surface-modified calcium salts in protein components

#### 3.1 Composite material of hydroxyl apatite and gelatin Bloom 300

[0058] First, solutions A and B were produced separately.

##### Solution A

[0059] 25.4 g of calcium nitrate tetrahydrate and 8.50 g diammonium hydrogen phosphate were each dissolved in 100 g deionized water. The two solutions were combined with formation of a white precipitate. After adding 10 ml of a 37% by weight HCl a clear solution is obtained.

##### Solution B

[0060] 200 ml deionized water, 200 ml 25% by weight aqueous ammonia solution and 20 g Plantacare<sup>R</sup> 1200 were combined and cooled in

an ice bath to 0°C.

[0061] With the formation of a hydroxyl apatite precipitate, solution A was added to solution B with vigorous stirring. After removing the excess ammonia the dispersion was purified by means of dialysis. On a rotary evaporator the dispersion was concentrated by evaporation by determining the separated amount of water to such an extent that the solid proportion in the dispersion, computed as hydroxyl apatite, was 7.5% by weight.

[0062] This dispersion was added at room temperature to 100 ml of a 10% by weight aqueous solution of gelatin Bloom 300 (manufacturer: Fluka) which was produced analogously to Example 1.1, then heated to 80°C and stirred for 5 minutes at this temperature. Then the mass was allowed to solidify with the formation of the composite material at room temperature.

#### 4. Production of adhesive dental films

##### 4.1 PVAc/HPC film

[0063] A dispersion of the composite material in an aqueous-alcohol solution of polyvinyl acetate and hydroxypropyl cellulose of the following composition was produced.

Polyvinyl acetate (MG 172000)	5% by weight
Hydroxypropyl cellulose	5% by weight
Water	9% by weight
Methanol	80% by weight
Composite material	1% by weight

[0064] The dispersion was poured in a 2 mm thick layer onto a silicone-coated base and dried. A roughly 0.2 mm thick film was obtained which was cut into strips 1 cm wide.

#### 4.2 Gelatin film

Gelatin hydrolysate	10.0% by weight
Composite material according to example 3.1	1.0% by weight
Ethanol	45.0% by weight
Water	35.0% by weight
Galloyl gallic acid	9.0% by weight

[0065] The dispersion was poured in a 2 mm thick layer onto a silicone-coated base and dried. A roughly 0.2 mm thick film was obtained which was cut into strips roughly 1 cm wide.

## Claims

1. Adhesive dental film for local, remineralizing treatment of teeth, consisting of a carrier material which can dissolve or swell in water and which adheres to the tooth, and the active ingredients intercalated therein, characterized in that as the active ingredient a fine-particulate calcium salt which is poorly soluble in water, selected from phosphates, fluorides, fluorophosphates and mixtures thereof, which optionally also comprises hydroxyl ions, carbonate ions or chloride ions, is contained.

2. Adhesive dental film as claimed in Claim 1, wherein the fine-particulate, poorly water-soluble calcium salt is chosen from hydroxyl apatite, fluorapatite and mixtures thereof.

3. Adhesive dental film as claimed in one of Claims 1 or 2, wherein the fine-particulate calcium salt has an average particle fineness of 10 - 300 nm (nanometers).

4. Adhesive dental film as claimed in one of Claims 1-3, wherein furthermore a protein component, selected from proteins, protein decomposition products and derivatives of proteins or protein decomposition products, is contained.

5. Adhesive dental film as claimed in one of Claims 1-4, wherein as the active ingredient a composite material of calcium salt which is poorly soluble in water, and a protein component, selected from proteins, protein decomposition products and derivatives of proteins or protein decomposition products, is contained.

6. Adhesive dental film as claimed in Claim 4 or 5, wherein the protein component is selected from gelatin, casein, their hydrolysates and mixtures thereof.

7. Adhesive dental film as claimed in one of Claims 4-6, wherein the protein component is contained in an amount of at least 0.1% by weight, preferably 1-10% by weight.

8. Adhesive dental film as claimed in one of Claims 1-7, wherein as the carrier material a water-soluble or water-swellaable natural or synthetic polymer material, selected from plant and microbial gums, cellulose ethers, copolymers of acrylic or methacrylic acid and esters of acrylic or methacrylic acid, polyvinyl alcohol, partially saponified polyvinyl acetate, polyvinyl pyrrolidone and mixtures thereof, is contained.